

VIBRATIONALLY RESOLVED PHOTOELECTRON ANGULAR DISTRIBUTIONS FOR  $\text{H}_2^+$ E.D. POLIAKOFF<sup>‡</sup>, J.L. DEHMER, P.M. DEHMER*Argonne National Laboratory, Argonne, Illinois 60439, USA*

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The photoelectron asymmetry parameter,  $\beta$ , is reported for individual vibrational levels of  $\text{H}_2^+(\text{X}^2\Sigma_g^+)$  formed by photoionization of  $\text{H}_2(\text{X}^1\Sigma_g^+)$  at wavelengths of 736, 584, 461 and 304 Å. At 584 Å,  $\beta$  exhibits a monotonic increase with vibrational quantum number (decreasing photoelectron kinetic energy) confirming the trend predicted by Itikawa.

## 1. Introduction

Photoionization of  $\text{H}_2$  is the natural prototype for the study of molecular photoionization dynamics, since the simplicity of its molecular structure permits quantitative and insightful theoretical analyses of a wide variety of ionization phenomena [1–19]. Photoelectron angular distributions are being used increasingly as a probe of molecular photoionization, since they are sensitive to both the dipole amplitudes and the relative phases of alternative ionization channels [2,3,7–11,13,20–30]. It has recently been pointed out that various resonant processes (e.g. shape and autoionization resonances) can induce sharp spectral variations in the photoelectron asymmetry parameter,  $\beta$ , and that these spectral variations are strongly dependent on the final vibrational state of the molecular ion [9–11,24–26]. This results from a breakdown of the Franck–Condon approximation. However, Itikawa [12–15,23] has noted that resonances need not be the only cause of such effects, since the dependence of the photoionization cross section on electron kinetic energy and inter-

nuclear separation,  $R$ , also results in a dependence of  $\beta$  on the final vibrational state of the ion. Itikawa's calculations indicate that, for  $\text{H}_2$ ,  $\beta(v)$  increases monotonically with vibrational quantum number ( $v$ ) of the ion at a given photon energy. Earlier experimental work on this point has not yielded a clear consensus [27–29], although the general phenomenon described by Itikawa has been noted and discussed by Mintz and Kupperman [30] and confirmed by Kreile and Schweig [28] for the  $\text{A}^2\Pi_u$  state of  $\text{N}_2^+$ .

It is this non-resonant dependence of  $\beta$  on the final vibrational state of the ion that we sought to investigate in this work, both for its intrinsic value and as a point of reference for studies of resonant effects. Results are presented at four photon energies: 16.85 eV (NeI, 736 Å); 21.22 eV (HeI, 584 Å); 26.91 eV (NeII, 461 Å); and 40.78 eV (HeII, 304 Å), and are discussed in the context of recent experiment and theory. It should be noted that a complementary dynamical parameter, namely the vibrational branching ratio, has been investigated previously both theoretically [31,32] and experimentally [33–35], and the results have confirmed Itikawa's prediction [13–15] of non-resonantly induced deviations from Franck–Condon vibrational intensities. The present work extends these investigations by demonstrating the effect on the angular distribution asymmetry parameter  $\beta$ .

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## 2. Experimental

The experimental apparatus has been described in detail elsewhere [36]. The main components are a hollow-cathode discharge lamp and a rotatable 5.1 cm mean radius hemispherical electron spectrometer with 0.10 cm diameter entrance and exit slits. Pass energies of 2 and 5 eV were used resulting in electron energy resolutions of 23 and 55 meV, respectively. An effusive gas jet was used to ensure that there was no alignment of the target molecules [37]. Spectra were recorded for electrons ejected at 90° and 40° relative to the photon propagation vector to determine the angular asymmetry parameter  $\beta$ , which is defined by the general form of the equation giving the angular distribution of electrons resulting from dipole excitation of a randomly oriented target by unpolarized radiation

$$d\sigma/d\theta = (\sigma_{\text{tot}}/4\pi)[1 - \frac{1}{2}\beta P_2(\cos\theta)].$$

Here  $\sigma_{\text{tot}}$  is the total photoionization cross section,  $P_2$  is the second Legendre polynomial, and  $\theta$  is the angle of electron ejection measured relative to the propagation direction of the light. The rotating spectrometer system was calibrated for asymmetry of the source geometry in the standard manner using the rare gases [28,38,39]. The specific calibrant and the value of  $\beta$  used at each wavelength are given in table 1.

## 3. Results and discussion

The results are presented for all four wavelengths in table 2, and are plotted for all wavelengths except

Table 1  
Angular calibration data

Line	$\lambda$ (Å)	Calibrant	State(s)	Assumed $\beta$
Ne I	736	Ar	$2P_{3/2}^0$	0.12 [38]
He I	584	Ar	$2P_{3/2}^0$	0.93 [28]
			$2P_{1/2}^0$	0.92 [28]
		Kr	$2P_{3/2}^0$	1.30 [28]
			$2P_{1/2}^0$	1.23 [28]
Ne II	461	Ar	$2P_{3/2}^0$	1.35 [39]
He II	304	Kr	$2P_{1/2}^0$	1.93 [39]

Table 2  
Vibrationally resolved  $\beta$  values for H<sub>2</sub> a)

$v$	HeI, 304 Å		NeI, 461 Å		HeI, 584 Å		NeI, 736 Å	
	present work	ref. [29]	present work	ref. [15]	present work	ref. [28]	present work	ref. [13] c)
0	1.78(13)	—	1.66(10)	1.80	1.65(6)	1.76(4)	1.67(6)	1.69
1	1.71(9)	1.7(2)	1.68(10)	1.81	1.69(6)	1.82(4)	—	1.75
2	1.82(10)	1.7(2)	1.78(10)	1.82	1.74(7)	1.87(5)	—	1.78
3	1.84(10)	1.7(2)	1.73(10)	1.84	1.77(6)	1.88(5)	—	1.82
4	1.81(10)	—	1.74(10)	1.85	1.78(4)	1.87(4)	—	1.84
5	—	—	1.67(10)	1.86	1.81(2)	1.89(3)	—	1.85
6	—	—	1.73(10)	1.88	1.85(2)	—	—	—
7	—	—	—	1.89	1.82(5)	—	—	—
8	—	—	—	1.90	1.88(10)	—	—	—
							ref. [14] d)	ref. [13] c)
							1.76	1.69
							1.79	1.75
							1.82	1.78
							1.84	1.82
							1.86	1.84
							1.88	1.85
							1.89	—
							1.90	—
							1.91	—

a) Numbers in parentheses refer to error ( $\pm$ ) in last digit.

b)  $\beta$  values for  $v = 0, 1$  and  $v = 3-7$  estimated from  $I(20^\circ)/I(90^\circ)$  ratios.

c) p wave only. d) p and f waves.

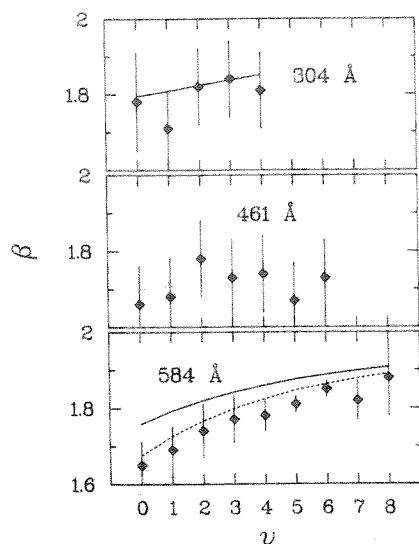


Fig. 1. Vibrationally resolved  $\beta$  values for photoionization of  $H_2$  at the indicated wavelengths. At 584 Å, the solid line (—) shows the results of the calculations of Itikawa which included both p- and f-wave contributions to the photoelectron wavefunction [14]. The dashed line (---) shows the results of the calculations which included only p-wave contributions [13]. At 304 Å, the solid line shows the results of the calculations which included both p-wave and f-wave contributions to the photoelectron wavefunction [15].

NeI in fig. 1. The  $\beta(v)$  results obtained with HeI excitation (584 Å) exhibit a monotonic increase with increasing  $v$ , with a slope that agrees very well with that predicted by Itikawa [13–15]. Hence, the present results confirm Itikawa's estimate of the non-resonant kinetic energy and  $R$  dependence of the complex dipole amplitude, which together result in a  $v$  dependence of  $\beta$ . The error bars of the present data encompass the results of Itikawa's calculations using only the p wave [13] and are never more than 0.05  $\beta$  units below the results of the calculations using p wave plus f wave [14]. The error bars presented for this work indicate the observed total variation of  $\beta$  for several measurements, and are somewhat larger than the statistical deviations for the measurements. Thus, the data are presented conservatively. It is important to seek the source of the residual disagreement between experiment and theory, particularly since the addition of higher partial waves should tend to improve the calculated results. The present values also are in reasonable agreement with earlier data by Krei-

and Schweig [28], Katsumata et al. [29], and Carlson and Jonas [27]. Although the present data tend to be slightly lower than earlier data, in most cases the agreement among all three data sets never exceeds the combined uncertainties by more than 0.03  $\beta$  units. Only in the present work, however, does the systematic trend in  $\beta(v)$  emerge with clarity.

The results obtained with HeII excitation (304 Å) are in good agreement with Itikawa's predictions [15], and are consistent with the results of Katsumata et al. [29]. The present work is an improvement over the earlier studies by Katsumata et al. in that the experimental uncertainties in the  $\beta$  values have been reduced by a factor of two and more vibrational levels have been measured. The observed trend in  $\beta$  versus  $v$  appears to agree well with that predicted by Itikawa [15]; however, the lower HeII light flux and the smaller photoionization cross section at the HeII excitation energy considerably increase the experimental uncertainties relative to the HeI measurements, preventing a definitive test of the predicted slope of  $\beta$  versus  $v$ .

The measurements made with NeI (or NeII excitation, see below) were more difficult to analyze than those made with HeI or HeII excitation. For NeI excitation, the rare-gas  $\beta$  values are rapidly varying and are poorly characterized. Furthermore, the  $H_2$  spectra resulting from the two components of the NeI doublet overlap above  $v = 0$ . Hence, for NeI, only the  $\beta$  value for  $v = 0$  determined at 736 Å is reported; however even the determination of this single value is significant since photoelectron measurements of  $H_2$  at the NeI excitation wavelength (736 Å) are of great interest for both theoretical and experimental reasons. First, since the photoelectrons have very little kinetic energy to overcome centrifugal barriers, the photoelectron is nearly a pure p wave [2]; second, the energy spacing of rotational branches in the photoelectron spectrum is on the order of tens of millivolts, which can be resolved by electron energy analyzers; and third, the photoelectrons have an inherently low-energy spread since the Doppler contribution is significantly reduced [40]. These factors have resulted in many studies of photoionization of  $H_2$  at 736 Å aimed at determining  $\beta$  values [2,9,13,14,16–18,41–43] and these studies are summarized in table 3. In general, the agreement between our measured value of  $\beta = 1.67 \pm 0.06$  and previous determina-

Table 3  
Comparison of  $H_2$   $\beta$  values obtained with NeI (736 Å) excitation

	Ref.	$\nu$	$\beta$
Theory	[2]	fixed $R$	1.71
	[9]	0	1.86
	[13]	0	1.69
	[14]	0	1.71
	[17]	fixed $R$	1.91
	[42]	fixed $R$	1.73
Experiment	[18] <sup>a)</sup>	1	1.87(1)
	present work	0	1.67(6)

<sup>a)</sup> From a re-evaluation of the data of Niehaus and Ruf [41].

tions is quite good; however, the disagreement with the MQDT prediction that  $\beta_{\nu=0} = 1.86$  is bothersome. The observed difference is not large, but, in comparisons with total photoionization cross sections [9–11], the MQDT has proven to be in excellent, quantitative agreement with experiment.

For NeII excitation, the hollow cathode discharge source produces many lines, resulting in multiple overlapping spectra. The analysis of this composite spectrum was performed by stripping the weaker intensity spectra from the highest-intensity one (461 Å). This was done in two steps. First, an Ar photoelectron spectrum was recorded and was analyzed in conjunction with the tabulated NeII emission line positions [44] to determine the relative intensities of the weaker emission lines. Second, using these experimentally determined emission line intensities, together with vibrational branching ratios at 584 Å [33–35], the weaker  $H_2$  spectra were simulated and then subtracted from the observed spectrum. Since the overlapping spectra stripped in this manner were weak relative to the residual 461 Å spectrum, errors in their estimation are diminished in the final result. Finally, the residual NeII spectrum was used to determine  $\beta(\nu)$  for the 461 Å excitation wavelength. The  $\beta$  values obtained from the present analysis are the only ones available at this wavelength.

At the NeII excitation wavelength (461 Å),  $\beta(\nu)$  does not increase monotonically with  $\nu$ . Previous work indicates that weak resonance excitation of doubly excited Rydberg states occurs in this spectral region [19], so that the purely non-resonant vibra-

tional dependence of  $\beta$  might be altered. However, the excursions from the predicted monotonic increase in  $\beta$  are small, and may result in part from errors arising from the analysis procedure in which the weaker spectra are stripped from the main photoelectron spectrum.

It is instructive to compare the present results with work that averages over the vibrational levels to determine the overall reliability of the present data. Two investigations have been carried out which have determined vibrationally averaged  $\beta$  values at the HeI excitation wavelength [45,46]. By taking a weighted average of our vibrationally resolved  $\beta$  values (using the relative vibrational intensities of Gardner and Samson [36] as weighting factors), the present results yield  $\bar{\beta} = 1.76 \pm 0.07$ , in excellent agreement with Southworth et al. [45] who obtained  $\bar{\beta} = 1.75 \pm 0.05$ . These values lie above that of Marr et al. [46] who obtained  $\bar{\beta} = 1.6 \pm 0.08$ ; however, we note that Marr et al. [47] used a lower value of  $\beta$  for the Ar calibrant than that used in the present work [28]. This is the probable cause for the discrepancy and reinforces the importance of explicitly stating the calibration standard used in all angular distribution measurements.

To summarize, we have presented new data on vibrationally resolved photoelectron angular distributions for photoionization of  $H_2$  at four discrete wavelengths. The  $\nu$  dependence at 304 Å is consistent with predictions by Itikawa, but the data are not of sufficient statistical certainty to confirm the weak, non-resonant  $\nu$  dependence of the theoretical predictions. At 584 Å, however, the data are adequate for this purpose, and, in fact, are the first data to confirm the smooth monotonic increase of  $\beta$  with increasing vibrational state of the ion (decreasing electron kinetic energy). The observation that the vibrational dependence of  $\beta$  at 584 Å agrees very well with the p-wave-only calculation, but is in poorer agreement with the p-wave plus f-wave calculation, is an unresolved problem at this time; however, it is significant to note that the monotonic trend and slope of both theoretical curves are confirmed by the present data.

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